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(54) HETEROGENEOUS CATALYST

(71) We, UNISEARCH LIMITED, a company limited by guarantee and incorporated under the laws of the State of New South Wales, Commonwealth of Australia, of 1 Barker Street, Kensington, New South Wales, Commonwealth of Australia, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a heterogeneous catalyst and to a process for the production thereof.

Homogeneous and heterogeneous catalysts have hitherto been regarded and treated as separate, although related aspects of the whole field of catalysts. The boundary between them has recently become blurred by the production of heterogenised homogeneous catalysts formed by the binding of a homogeneous catalyst to a heterogeneous substrate. As used in this specification the term "heterogeneous catalyst" is taken to include these catalysts formed by a process of heterogenising a homogeneous catalyst.

The present invention consists in a process for the production of a heterogenous catalyst suitable for the hydrogenation of organic molecules comprising the steps of:—

(a) irradiating a substrate selected from the group comprising a metal and an organic polymer with ionising radiation in the presence of an α olefin having the formula

$$X - R - \overset{\displaystyle H}{\overset{|}{C}} = CH_2$$

wherein R is an organic moiety containing a carbon chain of at least 2 carbon atoms or an aromatic group, and wherein X is a nitrogen or halogen containing group capable of coordinating with a metal salt or an organometallic complex, to graft the monomer to the substrate, and

(b) reacting the X group of the monomer-substrate conjugate with a catalytic metal salt or a catalytic organometallic complex, such that the monomer-substrate conjugate becomes a ligand of the metal salt or organometallic complex.

In another aspect the present invention consists in a process for the production of a hetereogenous catalyst for the hydrogenation of organic molecules comprising the steps of:—

(a) irradiating a substrate selected from the group comprising a metal and an organic polymer with ionising radiation in the presence of an α olefin having the formula

$$X - R - \overset{\displaystyle H}{\overset{|}{C}} = CH_2$$

wherein R is an organic moiety containing a carbon chain of at least two carbon atoms or an aromatic group, and wherein X is a nitrogen or halogen containing group capable of being chemically converted to a group capable of coordinating with a metal salt or an organometallic complex, to graft the monomer to the substrate.

(b) chemically converting the X group of the monomer-substrate conjugate to a group which is capable of coordinating with the metal salt or organometallic complex and,

(c) reacting the X group of the monomer substrate conjugate with a catalytic metal salt or a catalytic organometallic complex such that the monomer-substrate conjugate becomes a ligand of the metal salt of organometallic complex.

In a further aspect the present invention consists in a heterogeneous catalyst produced by a method according to this invention.

The process according to the present invention, and the catalysts resulting therefrom, have distinct advantages over the prior art. It is possible, using the present process, to attach an organo-metallic complex to a wider range of substrates. With at least some of the substrates the monomer graft only takes place on the external surfaces of the substrate such that

catalyst groups, when bound to the substrate, are always available to exert their catalytic action. The wider choice of substrates usable with the present invention allows the production of heterogeneous catalysts for use under physical conditions which would destroy conventional heterogenised homogeneous catalysts.

Catalysts according to the present invention may be used for the catalysis of a wide variety of reactions. A typical example might be the use of one of these catalysts for the hydrogenation of olefins.

In the process according to this invention the "ionising radiation" may comprise ionizing U.V. radiation, β-rays, γ-radiation, accelerated subatomic particles such as electrons, or radiation from other conventional ionising radiation sources, such as X-rays. The radiation dose and dose rate can be varied to vary the degree of monomer graft e.g. in the range 5 to 50% w/w and hence the degree of catalytic activity of the product.

The substrate is either metallic e.g. iron, copper or aluminium, or polymeric e.g. synthetic polymers such as polystyrene, polyethylene or polypropylene or natural polymers such as cellulose. If desired the substrate itself can be a copolymer.

The monomer is preferably an aromatic molecule bearing an active substituent. The most preferred monomers are p-nitro styrene and the nitro phenylacrylates. The presence of the aromatic ring or the carbon chain is thought to project the reactive group of the monomer from the surface of the polymer sufficiently for it to be readily accessible for reaction with the catalyst.

The term "active substituent" is taken to mean any substituent which can react with, or can be so converted as to react with the desired homogeneous catalyst.

If desired the reactive group on the monomer may be converted to another reactive group prior to the reaction with the homogeneous catalyst e.g. a nitro group might be converted to an amino group. In another embodiment of the invention an active group precursor on the grafted monomer may be converted to an active group prior to the reaction with the catalyst.

The homogeneous catalyst could be any one of a wide variety of metal based catalysts such as a metal salt or an organo-metallic complex. The so called "Wilkinson" catalysts are of particular applicability.

The invention may be put into practice in various ways and a number of specific embodiments will be described by way of example to illustrate the invention.

Example 1.

A 30% w/w solution of p-nitro styrene in methanol was added to a polypropylene powder and irradiated with γ-rays at a rate of 200,000 R/hr to give a total dose of .5MR. A 5% w/w graft of monomer to polymer was observed.

Rhodium tri-chloride was added to the prepared polymer with toluene and heated to 60°C and maintained for 1 hour. The product was washed in toluene and dried. The resulting heterogeneous catalyst was found to be an active hydrogenation catalyst.

Example 2.

Example 1 was repeated using dimethyl formamide as the solvent for the radiation induced grafting of the monomer to the polymer. The resultant heterogeneous catalyst was found to be suitable for use as a hydrogenation catalyst.

Example 3.

The graft copolymer produced in example 1 was subjected to a tin/hydrochloric acid reduction reaction to convert the active substituent of the copolymer from a nitro group to an amino group.

The reduced copolymer was reacted with rhodium trichloride as in example 1 and the resulting heterogeneous catalyst was found to be an active hydrogenation catalyst.

Example 4.

A 30% solution of p-chloro styrene in methanol was added to a polypropylene powder and irradiated with γ-rays at a rate of 200,000 R/hr to give a total dose of 5.MR. A 50% w/w graft of monomer to polymer was observed.

The copolymer was reacted with magnesium in ether to produce the corresponding Grignard reagent at the site of the active chloride atoms of the copolymer. The Grignard reagent was then reacted with rhodium (tris triphenyl phosphine) (carbonyl) chloride in tetrahydrofuran.

The heterogeneous catalyst so formed was found to be an active hydrogenation catalyst.

Example 5.

The reduced copolymer produced in example 3 was reacted with rhodium (tris triphenyl phosphine) (carbonyl) chloride in tetrahydrofuran to produce an active hydrogenation catalyst.

Example 6.

The process of example 4 was repeated using p-bromo styrene as the monomer.

The heterogeneous catalyst obtained was found to have hydrogenation reaction catalysing properties.

The hydrogenation catalyst activity of a variety of heterogeneous catalysts made in accordance with the invention was tested. The catalyst was shaken with toluene and cyclohexene under a positive head pressure of

hydrogen. The degree of hydrogenation of the cyclohexene was determined by measuring the drop in hydrogen pressure at varying temperatures. The results obtained are summarised in Table 1.

TABLE 1

Example	Catalyst	% v/v Hydrogenation	Tube	Temp.
1	p-NO_2 styrene/polypropylene + $RhCl_3$	0	1	50
	,,	0	2	120
	,,	17.8%	3	150
3	p-NH_2 styrene/polypropylene + $RhCl_3$	28.6	4	50
	,,	27.8	5	120
	,,	6.4	6	150
4	p-chloro-styrene/polypropylene + Rh (CO) $(Pph_3)_3Cl$	0	7	50
	,,	0.1	8	120
	,,	41.5	9	150
5	p-NH_2 styrene/polypropylene + Rh (CO) $(Pph_3)_3Cl$	24.6	10	50
	,,	24.0	11	120
	,,	29.5	12	150
control	p-NO_2 styrene/polypropylene Blank	0	13	150
control	p-NH_2 styrene/polypropylene ,,	0	14	150

WHAT WE CLAIM IS:—

1. A process for the production of a heterogenous catalyst suitable for the hydrogenation of organic molecules comprising the steps of:—

(a) irradiating a substrate selected from the group comprising a metal and an organic polymer with ionising radiation in the presence of an α-olefin having the formula

$$X - R - \overset{\displaystyle H}{\overset{|}{C}} = CH_2$$

wherein R is an organic moiety containing a carbon chain of at least 2 carbon atoms or an aromatic group, and wherein X is a nitrogen or halogen containing group capable of co-ordinating with a metal salt or an organometallic complex, to graft the monomer to the substrate, and

(b) reacting the X group of the monomer-substrate conjugate with a catalytic metal salt or a catalytic organometallic complex, such that the monomer-substrate conjugate becomes a ligand of the metal salt or organometallic complex.

2. A process for the production of a heterogenous catalyst for the hydrogenation of organic molecules comprising the steps of:—

(a) irradiating a substrate selected from the group comprising a metal and an organic polymer with ionising radiation in the presence of an α-olefin having the formula

$$X - R - \overset{\displaystyle H}{\overset{|}{C}} = CH_2$$

wherein R is an organic moiety containing a carbon chain of at least two carbon atoms or an aromatic group, and wherein X is a

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nitrogen or halogen containing group capable of being chemically converted to a group capable of coordinating with a metal salt or an organometallic complex, to graft the monomer to the substrate,

(b) chemically converting the X group of the monomer-substrate conjugate to a group which is capable of coordinating with the metal salt or organometallic complex, and

(c) reacting the X group of the monomer substrate conjugate with a catalytic metal salt or a catalytic organometallic complex, such that the monomer-substrate conjugate becomes a ligand of the metal salt of organo-metallic complex.

3. A process as claimed in claim 1 or claim 2 in which the substrate is selected from the group comprising iron, copper and aluminium.

4. A process as claimed in claim 1 or claim 2 in which the substrate is selected from the group comprising polystyrene, polyethylene, polypropylene and cellulose.

5. A process as claimed in claim 1 or claim 2 in which the monomer is selected from the group consisting of p-nitro styrene, a nitro phenylacrylate and p-chloro styrene.

6. A process as claimed in claim 1 or claim 2 in which the ionising radiation is selected from the group consisting of ionising U.V. radiation, β-rays, α-rays, accelerated sub-atomic particles and x-rays.

7. A process as claimed in claim 1 substantially as specifically described herein with reference to Examples 1 to 6.

8. A heterogenous catalyst produced by the process claimed in any one of the preceding claims.

9. In a process for the hydrogenation of an organic compound the improvement comprising the use, as a catalyst for the reaction, of a compound produced by a process comprising:—

(a) irradiating a substrate selected from the group comprising a metal and an organic polymer with ionising radiation in the presence of an α-olefin having the formula

$$X - R - \overset{\displaystyle H}{\overset{|}{C}} = CH_2$$

wherein R is an organic moiety containing a carbon chain of at least 2 carbon atoms or an aromatic group, and wherein X is a nitrogen or halogen containing group capable of coordinating with a metal salt or an organometallic complex, to graft the monomer to the substrate, and

(b) reacting the X group of the monomer-substrate conjugate with a catalytic metal salt or a catalytic organometallic complex, such that the monomer-substrate conjugate becomes a ligand of the metal salt or organometallic complex.

10. In a process for the hydrogenation of an organic compound the improvement comprising the use as a catalyst for the reaction of a compound produced by a process comprising:—

(a) irradiating a substrate selected from the group comprising a metal and an organic polymer with ionising radiation in the presence of an α-olefin having the formula

$$X - R - \overset{\displaystyle H}{\overset{|}{C}} = CH_2$$

wherein R is an organic moiety containing a carbon chain of at least two carbon atoms or an aromatic group, and wherein X is a nitrogen or halogen containing group capable of being chemically converted to a group capable of coordinating with a metal salt or organometallic complex, to graft the monomer to the substrate,

(b) chemically converting the X group of the monomer-substrate conjugate to a group which is so capable of coordinating with the metal salt or organometallic complex, and

(c) reacting the X group of the monomer substrate conjugate with a catalytic metal salt or a catalytic organometallic complex such that the monomer-substrate conjugate becomes a ligand of the metal salt or organometallic complex.

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